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Dimethyl and Methyl Hydrogen
Sulfate in the Atmosphere

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DIMETHYL AND METHYL HYDROGEN SULFATE IN THE ATMOSPHERE

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IN THE ATMOSPHERE**

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A novel technique of using the sample tube penetration profile of trace reactive gases has been applied to the sampling and indirect identification of candidate species through their diffusion coefficients. Laboratory studies of trace dimethyl and methyl hydrogen sulfate flow and their deposition as sulfate to a nylon wall demonstrated that this system can be described theoretically by the modified Gormley-Kennedy equation. Atmospheric samples taken with the penetration sampler in Elkmont, Tennessee, Riverside, California, and Detroit, Michigan exhibited mass deposition spectra that correspond to those of dimethyl and methyl hydrogen sulfate. The profiles were used to estimate the apparent gaseous diffusion coefficient and ambient mass concentration. The estimated diffusion coefficients agree well with semi-empirical theoretical estimates from gas kinetic theory. The estimates of ambient mass of the trace sulfate gas equal or exceed the measurements of fine particulate sulfate; these two variables are not correlated.

DIMETHYL AND METHYL HYDROGEN SULFATE IN THE ATMOSPHERE

Introduction

Our present understanding of cultural emissions, transport, deposition, and effects of S compounds in industrial and downwind areas is based on the predominance of two species: gaseous SO_2 and particulate sulfates. The presence of a substantial fraction in these areas of the atmospheric species other than SO_2 and particulate sulfates may pose a cause to re-evaluate removal rates, ecological effects, and human health effects.

Dimethyl sulfate $(\text{CH}_3\text{O})_2\text{SO}_2$ and methyl hydrogen sulfate $\text{CH}_3\text{OHOSO}_2$ have been shown to be present in oil and coal ash and in power plant plumes¹⁻². The ratio of particulate $(\text{CH}_3\text{O})_2\text{SO}_2$ to total S (corrected for background SO_2 and particulate sulfates) increased with plume travel time for an oil³ and a coal⁴ fired power plant plume. This behavior is due to either the condensation of $(\text{CH}_3\text{O})_2\text{SO}_2$ emitted directly or its formation in the plume.

The existence of substantial concentrations of ambient gaseous sulfate (or sulfate producing) compounds has been reported by us⁵. The chemical species have been tentatively identified as $(\text{CH}_3\text{O})_2\text{SO}_2$ and $\text{CH}_3\text{OHOSO}_2$ through the exhibited gaseous diffusion coefficient⁵, and more recently through specific surface adsorption/reaction samplers⁶.

Here we present ambient sampling data for Riverside, California, Elkmont Tennessee, and Detroit, Michigan.

Experimental

The concentrations of specific trace gases are frequently determined by adsorption or reaction with selective solids, followed by extraction and chemical analysis. For a gas that reacts rapidly with the selective solid, additional indirect evidence supporting the identity of that gas can be obtained from its penetration profile through a tube whose inner wall is the selective (reactive) solid. The fractional penetration of a gas being removed by diffusion to a reactive wall is given by the modified Gormley-Kennedy⁷ equation:

$$c_x/c_0 = 0.819 \exp(-11.49Dx/Q) \quad (1)$$

where c_x = average concentration of reactive gas at point x

c_0 = concentration at inlet

D = gaseous diffusion coefficient of reactive gas

x = distance from inlet of tube

Q = sampling flow rate

The application of Equation 1 requires: (a) a well-developed laminar flow in the tube, and (b) that the rate of depletion be controlled only by the rate of diffusion (i.e., the wall must be a perfect sink for the reactive gas). Equation (1) is a truncated solution, and if applied at $x = 0$ yields the impossible result that 81.9% of the trace gas passes through the inlet. Thus, it may not be applied for c/c_0 greater than 0.819.

Equation 1 may be used to determine D by regressing measurements of c/c_0 and x at constant Q. Measurements of c/c_0 for a field sampler are impractical but c/c_0 can be obtained from measurements of the deposited trace gas mass (M_j) along discrete sections of the tube. The cumulative deposit of material (F_i) through i discrete sections is

$$F_i = \sum_{j=1}^i M_j \quad (2)$$

$$= A(1 - c_x/c_0) \quad (3)$$

$$= A[1 - 0.819 \exp(-11.49 Dx/Q)] \quad (4)$$

where A = total mass of trace reactive gas entering tube and x corresponds to the end point of M_i (the last section used to calculate F_i).

If the discrete sections are of uniform length (Δx), then Equation 4 may be expressed as

$$F_i = A[1 - 0.819 \exp(-11.49 D i \Delta x / Q)] \quad (5)$$

where $\Delta x = x/i$

The use of a uniform length leads to simplifications in the theoretical treatment.

The mass of the reactive trace gas deposited on section j is

$$M_{j=i} = F_i - F_{i-1}, \quad i > 1 \quad (6)$$

$$= 0.819 A [1 - \exp(11.49 D \Delta x / Q)] \exp(-11.49 D x / Q) \quad (7)$$

$$= K \exp(-11.49 D x / Q) \quad (8)$$

$$\ln M_j = \ln K - 11.49 D x / Q \quad (9)$$

$$\text{where } K = 0.819 A [\exp(11.49 D \Delta x / Q) - 1] \quad (10)$$

Equation 8 is a restatement of Equation 1 in terms of deposited mass on sections of uniform discrete length along the tube. The condition that i be greater than 1, in addition to the truncation problem previously identified, excludes the first section (M_1) from the regression of $\ln M_j$ and x to obtain D and A .

Fits of experimental data to Equation 10 should be performed by weighting $\ln M_j$ to reduce the influence of the more imprecise determinations⁸. The weighting factor we have used is

$$W_j = (M_j/s_j)^2 \quad (\text{where } s = \text{standard deviation}) \quad (11)$$

Also, the estimate of $\ln K$ permits an estimate of A .

Laboratory Studies

In our laboratory studies, gaseous $(\text{CH}_3\text{O})_2\text{SO}_2$ and $\text{CH}_3\text{OHOSO}_2$ have been observed to deposit on nylon films inserted in Teflon tubes. Table I presents typical cases that demonstrate these two species are deposited to nylon in accordance to Equation 9. We have not yet performed closely controlled repetitive experiments to obtain accurate values of D owing to problems in handling these two gases. However, these cases demonstrate that $(\text{CH}_3\text{O})_2\text{SO}_2$ and $\text{CH}_3\text{OHOSO}_2$ have penetration spectra that may be represented by a weighted fit to Equation 10. The values of the diffusion coefficient (D_0) for $(\text{CH}_3\text{O})_2\text{SO}_2$ and $\text{CH}_3\text{OHOSO}_2$ estimated from atomic volume correlations⁹ are 0.073 and 0.081 cm^2/sec , respectively.

TABLE I. Penetration spectra of $\text{CH}_3\text{OHOSO}_2$ and $(\text{CH}_3\text{O})_2\text{SO}_2$ in nylon lined tube.

Section No.	x, cm	M_i , nmol		
		$\text{CH}_3\text{OHOSO}_2$	$(\text{CH}_3\text{O})_2\text{SO}_2$	
1	10	38 ± 3	46 ± 3	94 ± 3
2	20	25 ± 3	56 ± 3	65 ± 3
3	30	14 ± 3	30 ± 3	51 ± 3
4	40	7 ± 3	22 ± 3	33 ± 3
5	50	7 ± 3	11 ± 3	23 ± 3
6	60	3 ± 3	3 ± 3	12 ± 3
passing		4 ± 3	17 ± 3	107 ± 3
Total		98 ± 8	168 ± 8	385 ± 8
P/P ₀ (relative atm. press.)		0.854	0.848	0.851

From fit to Equation 10:

D , cm^2/sec	0.110 ± 0.024	0.114 ± 0.012	0.076 ± 0.007
D_0 , cm^2/sec (a)	0.094 ± 0.024	0.097 ± 0.012	0.065 ± 0.007
λ , nmol	125 ± 5	280 ± 3	395 ± 3

a - corrected for pressure

Field Studies

The apparatus used for sampling in the ambient atmosphere is shown in Figure 1. A cyclone was used on the inlet of the sampler to remove super-micrometric particles; its collection efficiency for operation at 28 liter/min is about 80% for 2.5 μm diameter particles. The reactive section of the sampler was made by lining the Teflon carrier tube with nylon fiber mats (thickness = 0.15 mm). The internal diameter of the nylon-lined sections was 0.76 cm. The Teflon tube was kept straight by inserting it into a close-fitting rigid steel tube. Since well-developed laminar flow is a necessary condition at the entrance to the reactive zone, a 25-cm section of inert Teflon was left ahead of the nylon section. The parabolic flow velocity is fully established at 21 cm for a flow rate of 25 cm^3/sec , which corresponds to a Reynolds number of 280. Also, a 14 cm bare section of Teflon tubing was left downstream of the nylon to prevent disturbance of the flow profile in the reactive section. A Teflon filter holder with a 47-mm Teflon filter (1- μm FALP Millipore) was used to trap the particles exiting the tube sampler.

Chemical Analysis

After each field experiment, the nylon filter mats were removed and cut into 8 sections, each 5.00 ± 0.05 cm long. Each one was extracted in 10 $\mu\text{g}/\text{cm}^3$

of aqueous 0.003M NaHCO_3 and 0.0024M Na_2CO_3 , which was the carrier solution used for the ion chromatographic analysis. The time period between sample collection and extraction was 3 to 15 days. The extraction was expedited by using vortex agitation. Ion peaks were integrated and concentrations calculated based on $0.5 \mu\text{g}/\text{cm}^3$ calibration standards. The standard deviation for replicates over the range of observed concentrations of sulfate is $0.02 \mu\text{g}/\text{cm}^3$ ($0.2 \mu\text{g}/\text{section}$) or $\pm 2\%$, whichever value is larger. Typically, the background of sulfate was $0.2 \mu\text{g}/\text{section}$, but on a few occasions, it was twice this value.

Results

Ambient atmospheric samples were collected at three locations: (a) Elkmont, Tennessee, which is a rural area in the Smoky Mountains, (b) Riverside, California, which is a photochemically active area downwind of Los Angeles, and (c) downtown Detroit, Michigan.

Elkmont, Tennessee

The samples were collected during the period 21-27 March 1980, with a simpler version of the apparatus shown in Figure 1. The cyclone was not used, and the Teflon tube inlet was oriented either to face up or down. The tube was operated in a Hi-Vol shelter to reduce the sampling of supermicrometric particles. Also, the flow rate for these samples only was $8.33 \text{ cm}^3/\text{sec}$.

The weighted sulfate masses of the sections were fit to Equation 10, and the results of the estimates of $\bar{D}$ and A are given in Table II. The average value of $\bar{D}$ was computed by weighting with the variance:

$$\bar{D} \pm \bar{s} = \sum(D_i/s_i^2) \pm \sum(1/s_i^2)^{0.5} \quad (12)$$

The influence of altitude on $\bar{D}$ was removed by correcting to standard pressure with the relationship

$$D_0 = D(P/P_0) \quad (13)$$

where P/P_0 is the relative atmospheric pressure.

Riverside, California

The samples were collected during the period 12 September through 3 October 1980, using the apparatus shown in Figure 1. The site was the Statewide Air Pollution Research Center, Fawcett Laboratory, Riverside, California. The flowrate through the nylon-lined Teflon tube was $25 \text{ cm}^3/\text{sec}$. The weighted sulfate masses of the sections were fitted to Equation 10, and the results of the estimates of $\bar{D}$ and A are given in Table III. The average value of $\bar{D}$ was obtained using Equation 12. No correction for pressure was made.

Detroit, Michigan

The samples were collected during the period 28 July through 21 August 1981 in downtown Detroit, Michigan. The apparatus used is shown in Figure 1. The flowrate through the nylon-lined Teflon tube was $25 \text{ cm}^3/\text{sec}$. The weighted sulfate masses of the sections were fitted to Equation 10. The results of the estimates of $\bar{D}$ and A are given in Table IV. The average value of $\bar{D}$ was obtained using Equation 12. No correction for pressure was made.

Discussion

The weighted values of the diffusion coefficient of the gaseous sulfate species observed and those estimated for $(\text{CH}_3\text{O})_2\text{SO}_2$ and $\text{CH}_3\text{OHOSO}_2$ from semi-empirical theory are given in Table V. The agreement between the observed and theoretical values of likely candidates is good. The experimental values may be slightly low due to the small quantity of SO_2 adsorbed and particulate sulfate deposited uniformly to the nylon. This deposition leads to positive deviations to the deposition spectra that increase as distance increases along the tube. In almost all cases, such positive deviations were observed, but they were minimized by weighting the values of $\ln M_i$ by W_i (given by Equation 11). The influence of this behavior is to decrease the estimate of D and increase its standard deviation. The deposition of reactive gases of molecular weight less than that of $\text{CH}_3\text{OHOSO}_2$ will give positive deviations that decrease as distance increases along the tube. The weighting procedure greatly magnifies the contribution of this interfering species, leading to an increase in the estimate of D and standard deviation expected for only $\text{CH}_3\text{OHOSO}_2$ and $(\text{CH}_3\text{O})_2\text{SO}_2$. There were cases for D greater than 0.100, which may be due to reactive compounds with molecular weight less than that of $\text{CH}_3\text{OHOSO}_2$.

The estimated average mass of the reactive sulfate gas and the measured values of fine particulate sulfate mass are compared in Table VI. The average mass concentrations of the reactive gas for the Elkmont and Riverside studies are approximately equal to those for the fine particles. The reactive gas concentrations in downtown Detroit is greater than that for the fine particles. Thus, relative to urban and rural fine particulate sulfate, the reactive gas appears to be at least as important in regard to contribution to the atmospheric sulfur burden. The correlation of the reactive sulfate gas and the fine particulate sulfate was poor, as can be seen from the values of the correlation coefficient in Table VI. Therefore, it is unlikely that the major reactions for forming the sulfate gas are embedded in those governing the formation of sulfate. It is not reasonable at this time to postulate atmospheric formation pathways for $\text{CH}_3\text{OHOSO}_2$ and $(\text{CH}_3\text{O})_2\text{SO}_2$. Also, nothing is known of their removal pathways.

Conclusion

Our results indicate the presence of gaseous sulfate (or sulfate forming) species in the atmosphere with diffusion coefficients in the range of about 0.05 to 0.08 cm^2/sec . $(\text{CH}_3\text{O})_2\text{SO}_2$ and $\text{CH}_3\text{OHOSO}_2$ have been shown in the laboratory to react rapidly with nylon and yield sulfate on prolonged extraction. These species have semi-empirical theoretical diffusion coefficients within this range. Since independent sampling methods indicate the presence of these two species at comparable concentrations, these two are likely candidates to be the reactive gaseous sulfate compounds.

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TABLE II. Estimate of D and A of reactive gaseous sulfate species: Elkmont, Tennessee
(March 1980)

No.	Day	Time, CDT	Δ Time, min	Volume, m ³	$D \pm s$, cm ² /sec	$(A \pm s)/\text{Volume}$ $\mu\text{g}/\text{m}^3$ (a)	Inlet facing
1	20/21	15:30-11:30	1200	0.600	0.051 ± 0.026	6.5 ± 2.6	down
2a	21/22	15:00-15:00	1440	0.720	0.052 ± 0.015	9.9 ± 1.2	down
b	21/22	15:00-15:00	1440	0.720	0.119 ± 0.054	5.7 ± 1.1	up
3a	22/23	15:20-14:20	1380	0.690	0.044 ± 0.039	3.7 ± 4.2	down
b	22/23	15:20-14:20	1380	0.690	0.037 ± 0.043	3.5 ± 6.2	up
4	23/24	15:00-15:00	1440	0.720	0.043 ± 0.026	5.5 ± 2.6	down
5a	24/25	15:40-15:40	1440	0.720	0.097 ± 0.038	7.4 ± 1.1	down
b	24/25	15:40-15:40	1440	0.720	0.108 ± 0.057	4.9 ± 1.4	up
6a	25/26	16:00-14:00	1320	0.660	0.055 ± 0.050	3.9 ± 3.8	down
b	25/26	16:00-14:00	1320	0.660	0.083 ± 0.031	6.9 ± 1.3	up
7a	26/27	14:00-12:00	1320	0.660	0.129 ± 0.034	11.2 ± 0.7	down
b	26/27	14:00-12:00	1320	0.660	0.157 ± 0.053	11.5 ± 0.7	up
8	27/28	12:40-11:40	1380	0.690	0.048 ± 0.021	9.0 ± 1.8	down
$\bar{D} \pm \bar{s}$:					0.063 ± 0.008		
$D_0 \pm s$:					0.056 ± 0.008		

a. Expressed as mass of sulfate

TABLE III. Estimate of D and A of reactive gaseous sulfate species:
Riverside, California (September and October 1980)

No.	Day	Time	Δ Time, min	Volume, m^3	$D \pm s$, cm^2/sec	$(A \pm s)/Volume$ $\mu g/m^3$ ^a
<u>September:</u>						
1	12	0000-2400	1440	1.08	0.111 ± 0.018	12.9 ± 0.6
2	13/14	1130-1130	1440	1.08	-0.048 ± 0.074^b	-0.4 ± 13.4^b
3	15/16	1200-1200	1440	1.08	0.080 ± 0.008	30.2 ± 0.4
4	17	0000-2400	1440	1.08	0.103 ± 0.011	21.7 ± 0.4
5	22/23	0730-0730	1440	1.08	0.112 ± 0.010	23.3 ± 0.3
6	24/25	0730-0730	1440	1.08	0.075 ± 0.005	49.2 ± 0.3
7	25/26	0730-0730	1440	1.08	0.081 ± 0.006	41.9 ± 0.3
8	26/27	0730-0730	1440	1.08	0.110 ± 0.006	39.5 ± 0.2
9	27/28	0730-0730	1440	1.08	0.122 ± 0.018	13.9 ± 0.5
10	28/29	0730-0730	1440	1.08	0.090 ± 0.009	25.6 ± 0.4
11	29/30	0730-0730	1440	1.08	0.054 ± 0.004	59.6 ± 0.4
12	30/1	0730-0730	1440	1.08	0.050 ± 0.006	49.2 ± 0.6
<u>October</u>						
13	1/2	0730-0730	1440	1.08	0.077 ± 0.005	46.0 ± 0.3
14	2/3	0730-0730	1440	1.08	0.062 ± 0.007	37.8 ± 0.5
$\bar{D} \pm \bar{s}$:					0.076 ± 0.002	

a - Expressed as mass of sulfate

b - Data rejected

TABLE IV. Estimate of D and A of reactive gaseous sulfate species:
Detroit, Michigan (July and August 1981)

No.	Day	Time, CDT	Δ Time, min	Volume, m ³	D $\pm$ s, cm ² /sec	(A $\pm$ s)/Volume $\mu\text{g}/\text{m}^3$ a
<u>July</u>						
1a	28/29	0900-0930	1470	2.21	0.037 $\pm$ 0.006	27.4 $\pm$ 0.4
b	28/29	0900-0930	1470	2.21	0.046 $\pm$ 0.006	22.2 $\pm$ 0.4
2a	30/31	0945-0915	1410	2.12	0.101 $\pm$ 0.004	28.6 $\pm$ 0.1
b	30/31	0945-0915	1410	2.12	0.103 $\pm$ 0.005	24.4 $\pm$ 0.1
<u>August</u>						
3a	4/5	0930-0915	1425	2.14	0.077 $\pm$ 0.006	20.6 $\pm$ 0.2
b	4/5	0930-0915	1425	2.14	0.078 $\pm$ 0.006	25.5 $\pm$ 0.2
4a	5/6	0940-1055	1515	2.27	0.012 $\pm$ 0.002	178.9 $\pm$ 0.5
b	5/6	1940-1055	1515	2.27	0.024 $\pm$ 0.002	91.4 $\pm$ 0.3
5a	6/7	1055-0945	1370	2.06	0.046 $\pm$ 0.003	51.7 $\pm$ 0.2
b	6/7	1055-0945	1370	2.06	0.068 $\pm$ 0.003	40.4 $\pm$ 0.1
6a	10/11	1130-0935	1325	1.99	0.097 $\pm$ 0.005	23.5 $\pm$ 0.1
b	10/11	1130-0935	1325	1.99	0.078 $\pm$ 0.005	27.8 $\pm$ 0.1
7a	11/12	0950-0920	1410	2.12	0.085 $\pm$ 0.009	14.9 $\pm$ 0.2
b	11/12	0.50-0910	1410	2.12	0.074 $\pm$ 0.007	16.6 $\pm$ 0.2
8a	12/13	0945-1000	1455	2.18	0.089 $\pm$ 0.004	31.9 $\pm$ 0.1
b	12/13	0945-1000	1455	2.18	0.069 $\pm$ 0.003	38.0 $\pm$ 0.1
9a	13/14	1010-0920	1390	2.09	0.096 $\pm$ 0.007	17.1 $\pm$ 0.1
b	13/14	1010-0920	1390	2.09	0.111 $\pm$ 0.007	16.5 $\pm$ 0.1
10a	18/19	1030-0920	1370	2.06	0.071 $\pm$ 0.007	18.1 $\pm$ 0.2
b	18/19	1030-0920	1370	2.06	0.034 $\pm$ 0.006	32.1 $\pm$ 0.5
11a	19/20	0940-1030	1490	2.24	0.050 $\pm$ 0.004	32.7 $\pm$ 0.2
b	19/20	0940-1030	1490	2.24	0.009 $\pm$ 0.004	160 $\pm$ 1
12a	10/21	1045-0935	1370	2.06	0.052 $\pm$ 0.003	46.3 $\pm$ 0.2
b	10/21	1045-0935	1370	2.06	0.119 $\pm$ 0.006	27.6 $\pm$ 0.1
$\bar{D} \pm \bar{s}$:					0.050 $\pm$ 0.008	

a - Expressed as mass of sulfate

TABLE V. Observed weighted diffusion coefficients of gaseous sulfate species and theoretical values

<u>Observed</u>	<u>D, cm²/sec</u>
Elkmont, Tennessee	0.056 ± 0.008
Riverside, California	0.076 ± 0.002
Detroit, Michigan	0.050 ± 0.008
<u>Theory</u>	
(CH ₃ O) ₂ SO ₂	0.073 ± 0.010
CH ₃ OHOSO ₂	0.081 ± 0.010

TABLE VI. Comparison of sulfate reactive gas and fine particulate mass concentration

	<u>Sulfate mass, µg/m³</u>		<u>Correlation coefficient</u>
	<u>Reactive gas^a</u>	<u>Fine particles^b</u>	
Elkmont, Tennessee	6.9 ± 2.8	4.7 ± 3.1	0.23 (n = 13)
Riverside, California	34 ± 14	23 ± 10	-0.19 (n = 13)
Detroit, Michigan	28 ± 10	4.3 ± 1.8	0.35 (n = 24)

a. Estimated (values from Tables II - IV)

b. From experimental observations not presented in this paper

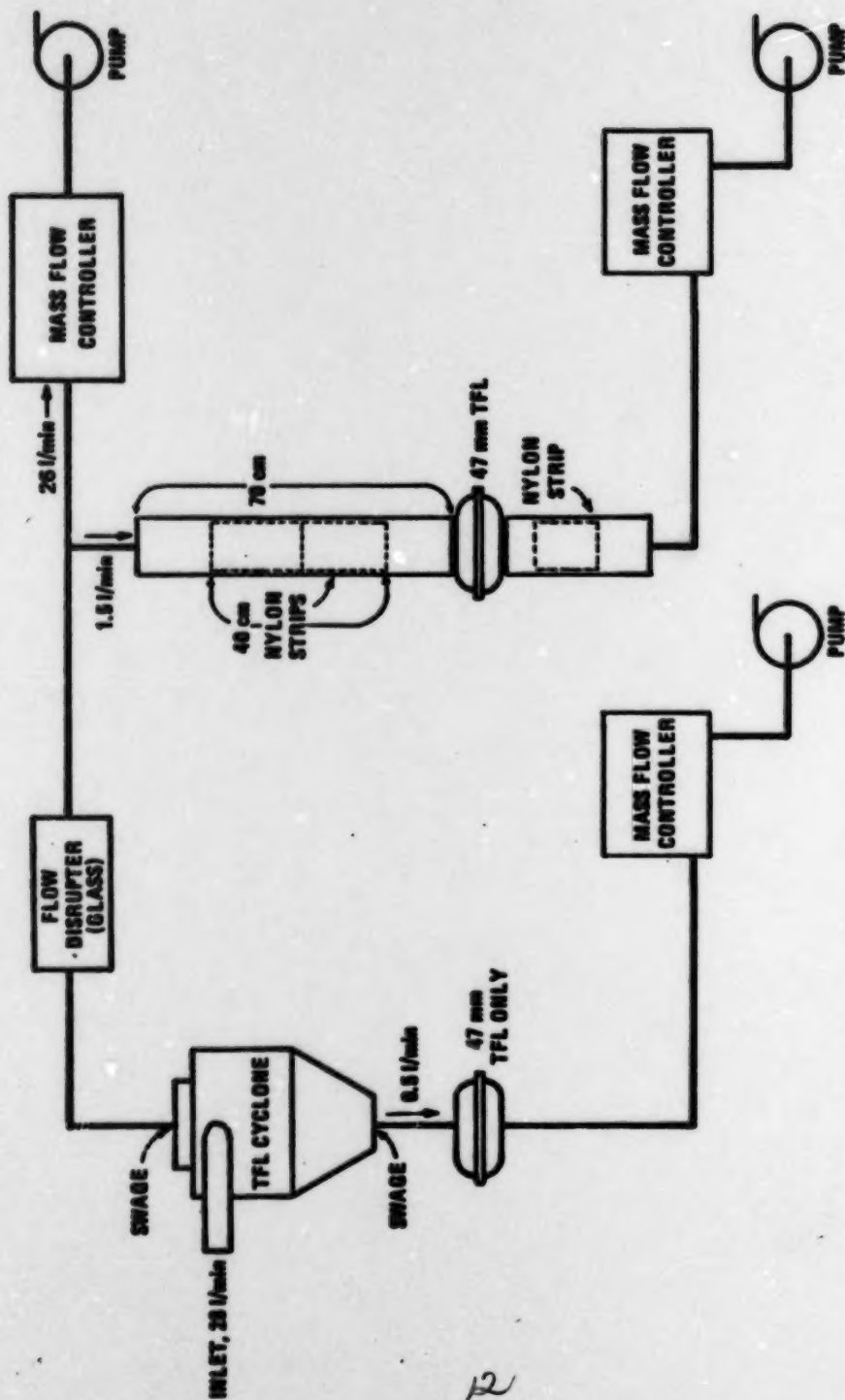


Figure 1. Apparatus for sampling trace reactive gases onto reactive tube walls. For sampling the gaseous sulfate species, 2 nylon strips (each 20 cm long) comprise the reactive wall. The 2 strips are butted against each other to give an effective length of 40 cm. The filter and downstream nylon strip samples are not used in the data analysis.